

Single Organic Molecules Designed as Nanoscale Connectors: Fullerene Isoxazoline Derivatives

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Recently a fullerene isoxazoline was reported as an example for nanoscale connectors in molecular electronic devices. The construction of nanoscale devices is a potentially important area of technology. By using the semiempirical PM3 calculation, we optimized the structures for two fullerene isoxazoline derivatives and thirteen regioisomers of the second addition of a nitrile oxide to a fullerene isoxazoline derivative. Our results suggest that fullerene isoxazoline derivatives could be used as nanoscale connectors with the possibility of attaching of spacer units in a specific angle arrangement.

Key Words : Regioisomers, Fullerene isoxazoline derivatives, Nanoscale connectors, PM3

Introduction

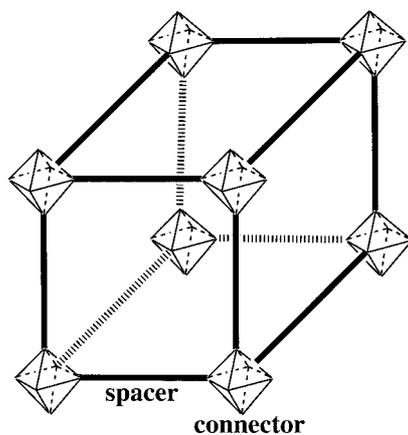
Molecular electronic devices are usually represented as 3-dimensional assemblies of electroactive units (as connector) separated by some rigid structure (as spacer) that can function as a “wire” (of a well-defined length) as shown in Scheme 1. In the area of spacer molecules, there are a number of alternative types available, including “[n] staffanes”¹ and “[n] ladderances”².

The essential characteristics required for the connector units are that they be electroactive and that they allow for the attachment of a number of spacer units. For a well-defined structure to be constructed, attachment of spacer units in a linear or specific angular arrangement is required. Octahedral metal complexes are the most often cited species as potentially filling the role of a connector.

Fullerenes can meet these requirements.³ Fullerenes have a number of redox states that are accessible in a reasonable

potential window, and with 30 double bonds available for a number of different angles of attachment of spacers. Recently the regiochemistry of the second addition of a nitrile oxide to a fullerene isoxazoline related to this field has been reported.³ Isoxazoline derivatives of C₆₀ by 1,3-dipolar cycloadditions of nitrile oxides to 6-6 double bonds of the fullerene has been also reported.^{4,5}

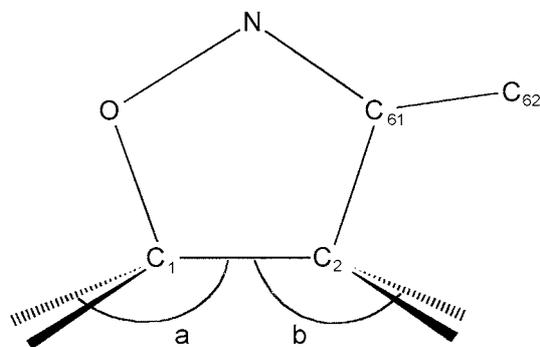
The purpose of this work is to explain approximately eight different regioisomers of C₆₀-PhCNO diadducts (designed as nanoscale connectors) observed in the photodiode array detection.³ We theoretically analyze twenty eight regioisomers of C₆₀-PhCNO diadducts by using the semiempirical PM3 calculation.⁶ Here the heterocycle is unsymmetrical, which imposes questions about regioisomers (which bond is attacked in the 2nd addition) depending on the orientation of the new heterocycle. We will discuss the possibility of C₆₀-PhCNO diadducts as a nanoconnector to allow the attachment of a number of spacer units in a specific angle arrangement.



Scheme 1. An assembly of “connectors” and rigid “spacers”: building blocks of molecular devices.

Models and Calculations

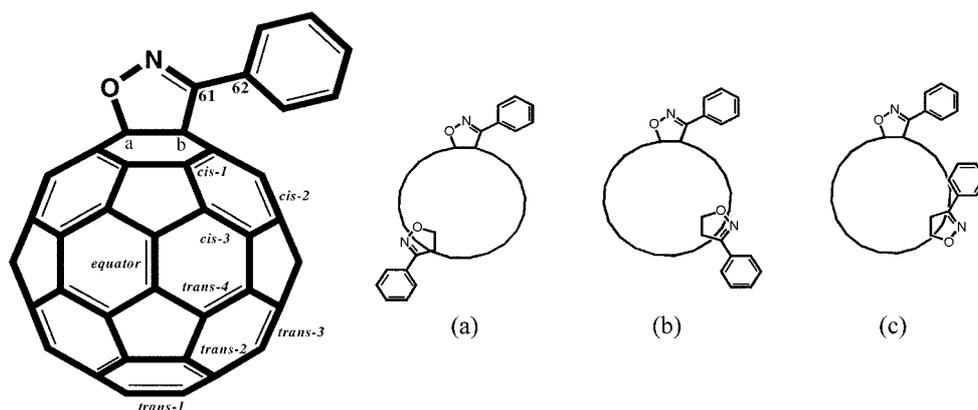
C₂H₄[MeCNO] (1), C₂H₄[PhCNO] (2), C₆₀[MeCNO] (3), C₆₀[PhCNO] (4), and C₆₀[PhCNO]₂ models are calculated by using the restricted Hartree-Fock (RHF) method with the



Scheme 2. The notations of atoms and the pyramidal angles of two carbon atoms attached by the nitrile oxide in ethylene and fullerene isoxazolines.

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Scheme 3. The fullerene isoxazoline, $C_{60}(\text{PhCNO})$, and eight regioisomers of its diadducts. (a) obtuse connections and (b) acute connections with the same rotational direction of two phenyl rings, and (c) acute connections with the opposite directions of two phenyl rings.

MNDO Hamiltonian with PM3 parameterization.⁵ No symmetry constraints were specified for the geometry optimizations and the SCF convergence criteria were 10^{-8} kcal/mol.

The atomic notation and the pyramidal angles near two carbon atoms bonded to the nitrile oxide in ethylene and fullerene are shown in Scheme 2.

Double addition of the nitrile oxides to C_{60} at six-six ring fusions forms eight regioisomers as shown in Scheme 3. For the description of spatial arrangements of the added groups, the C_{60} molecule is divided into three sections with regard to the location of the second attack. The 2nd addition can take place on the same hemisphere (*cis*), at the equator (*e*), or on the opposite hemisphere (*trans*). Three different sets of double bonds can be attacked within the same hemisphere (*cis-1*, *cis-2*, *cis-3*), and four different sets of double bonds are available on the opposite hemisphere (*trans-1*, *trans-2*, *trans-3*, *trans-4*).⁶

Diadducts ($C_{60}(\text{PhCNO})_2$) could be formed in two fashions because the first addition of benzonitrile oxide to C_{60} reduces the symmetry of C_{60} from I_h to C_s point group. Here, we considered five regioisomers with the second benzonitrile oxide on the opposite hemisphere (*trans-1*, *trans-2*, *trans-3*, *trans-4*) and at the equator (*e*). The *trans-2*, *trans-3*, and *trans-4* regioisomers have two kinds of isomers: The first form with two phenyl rings are at larger distances with an obtuse angle with respect to each other. The second form has two phenyl rings at an acute angle. Also the second addition of benzonitrile oxide to C_{60} has two possibilities depending on the directions of two phenyl groups.

Results and Discussion

Monoadducts. Table 1 shows the geometric parameters near the attached site in their optimized structures obtained from the PM3 calculations for $C_2H_4[\text{MeCNO}]$ (**1**), $C_2H_4[\text{PhCNO}]$ (**2**), $C_{60}[\text{MeCNO}]$ (**3**) and $C_{60}[\text{PhCNO}]$ (**4**). The length of the C1-C2 bond is obtained to be 1.322 Å in ethylene and 1.384 Å in C_{60} . The C1-C2 bond lengths of ethylene and fullerene have increased about 0.21 through the formation of isoxazolines. The C61-C62 bond length of the molecule **2** is shorter (0.019 Å) than that of the molecule **1** from cycloaddition reactions of nitrile oxides with ethylene. Also the C61-C62 bond length in **3** is longer (0.015 Å) than that in **4** (fullerene isoxazoline). This suggests that the C61-C62 bond has the resonance effect between the C61=N double bond and the phenyl ring. The pyramidal angles *a* and *b* in C_{60} isoxazolines are smaller than those in ethylene isoxazolines. The structural deformation of C_{60} frame is localized at the nearest neighbors of the sites attached through the formation of isoxazolines.

In the energetically optimized structure of **4** (see Schemes 2 and 3), the bond lengths (Å) are as follows: C1-C2, 1.594; C2-C61, 1.520; C61-C62, 1.465; C61-N, 1.303; N-O, 1.391; O-C1, 1.450. The calculated bond lengths are reasonable in comparison with the X-ray structure⁷ of 3-(9-anthryl)-4,5-dihydroisoxazole derivative of C_{60} . The plane of phenyl ring has the dihedral angle of 62° with the plane of C2C61C62. The calculated total energy difference between the optimized C_1 isomer and the C_s isomer with the phenyl plane perpendicular to the C2C61C62 plane is less than 0.1 kcal/

Table 1. The geometric parameters for the ethylene and fullerene isoxazolines obtained from PM3 calculations

Entry	Molecules	Bond Length						Pyramidal angle (°)	
		C1-C2	C1-O	C2-C61	O-N	C61-N	C61-C62	a	b
1	$C_2H_4[\text{MeCNO}]$	1.535	1.438	1.506	1.414	1.305	1.479	127.3	124.5
2	$C_2H_4[\text{PhCNO}]$	1.535	1.439	1.509	1.406	1.309	1.460	127.4	124.1
3	$C_{60}[\text{MeCNO}]$	1.591	1.449	1.517	1.395	1.303	1.480	123.4	123.5
4	$C_{60}[\text{PhCNO}]$	1.594	1.450	1.520	1.391	1.303	1.465	123.7	123.1

Table 2. Atomic charges for the isoxazoline molecules obtained from PM3 calculations

Molecule	Atomic Charges						q^* of C_2H_4 or C_{60}
	C1	C2	C61	C62	N	O	
1	0.018	-0.102	-0.140	-0.047	0.036	-0.190	0.176
2	0.018	-0.102	-0.090	-0.036	0.040	-0.185	0.182
3	0.151	0.051	-0.112	-0.055	0.060	-0.139	0.052
4	0.148	0.060	-0.069	-0.044	0.075	-0.139	0.060

* The charges transferred from C_2H_4 or C_{60} in the isoxazolines.

mol. The rotation barrier of phenyl is 1.6 kcal/mol. Thus, the result of this calculation suggests why the ^{13}C NMR spectrum of the isoxazoline derivative of C_{60} with propionitrile oxide⁴ shows C_s symmetry.

Table 2 shows the atomic net charges of the considered isoxazoline molecules and the charges transferred from ethylene or C_{60} . The charges transferred from C_2H_4 are much larger than those from C_{60} in the isoxazoline derivatives. It suggests that C_{60} is more electronegative than ethylene. The C61 and C62 in **1** have more (0.05 and 0.01) electronic charges than those in **2**. The difference of the net charges of C61 and C62 in **1** is 0.09, in **2** is 0.05. In the fullerene isoxazolines, the electronic charges of C61 and C62 are reduced by 0.04 and 0.01 as the methyl group is substituted by the phenyl group, the difference of the net charges of C61 and C62 in **3** is 0.06 and in **4** is 0.03.

The isoxazolines considered in this study showed that the charge transferred from the methyl group is larger than that from the phenyl group. In $C_2H_4[RCNO]$ ($R = Me$ or Ph) the net charge of C1 is positive and that of C2 is negative. But in $C_{60}[RCNO]$ ($R = Me$ or Ph) both the C1 and the C2 have positive net charges. The variation of the net charges in C_{60} frame through the formation of isoxazolines is localized at the attached carbon atoms in the 6-6 bond and their nearest neighbors. This result has been reported in other studies for fullerene derivatives.^{8,9} And this means the localized geometric deformation of C_{60} frame.

And then we considered the effects on the stability and the properties of **2** and **4** with the change of dihedral angle between the phenyl ring and the C-N-O plane. The differences between the atomic net charges of C61 and C62 in the both of $C_2H_4[PhCNO]$ and $C_{60}[PhCNO]$ are smaller at the dihedral angle of 0° than those at the other dihedral angles. It suggests the resonance effect be in the C61-C62 bond. Figure 1(a) shows the relative repulsive, electronic and total energies of $C_2H_4[PhCNO]$ at each dihedral angle. The repulsive energy is the highest and the electronic energy is the lowest at the dihedral angle of 0° . But this case is energetically most stable. The resonance effect on the stability is slightly more considerable than the steric effect. The relative energies of $C_{60}[PhCNO]$ in Figure 1(b) show that the trend of the electronic and repulsive energies in $C_{60}[PhCNO]$ is opposite to that in $C_2H_4[PhCNO]$. Its tendency of $C_{60}[PhCNO]$ would be caused by the resonance and the steric effect of C_{60} frame.

We studied the geometric parameters of $C_2H_4[PhCNO]$ and $C_{60}[PhCNO]$ depending on the rotation of the phenyl

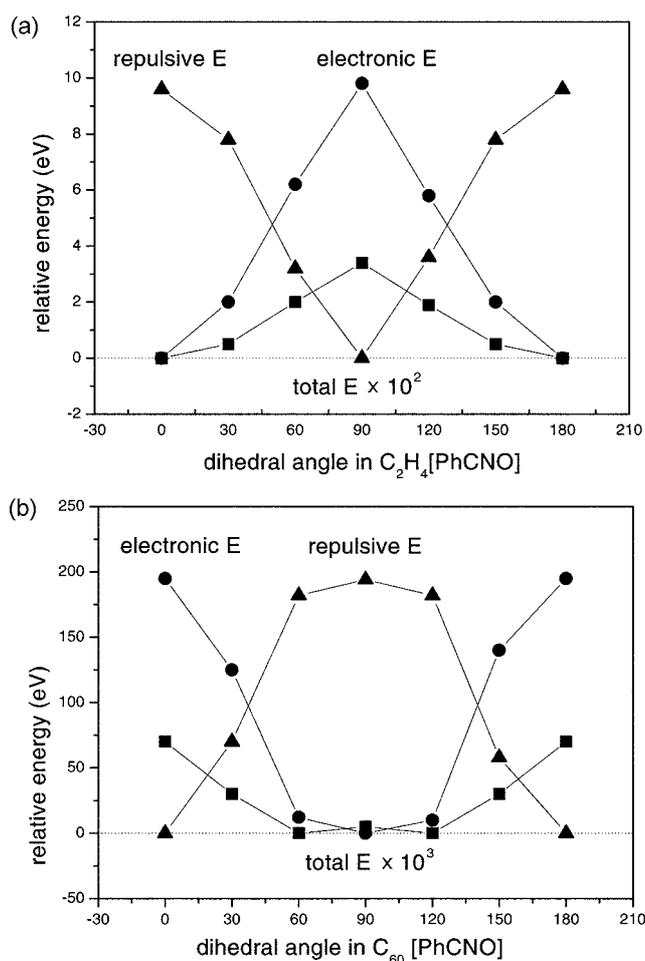


Figure 1. The relative repulsive (\blacktriangle), electronic (\bullet) and total energies (\blacksquare) at each dihedral angle between the phenyl ring and the CNO planes: of $C_2H_4[PhCNO]$ (a) and of $C_{60}[PhCNO]$ (b).

group. The variations of the C61-C62, C61-N, and N-O bond lengths with the rotation of the phenyl ring are slightly larger than those of the other bonds in $C_2H_4[PhCNO]$. So it is clear that the resonance effect on the stability is larger than the steric effect in this molecule. At the dihedral angle of zero the C61-C62 distance is the shortest and the C61-N bond is the longest, and then the steric effect and the resonance stability are the largest. But in the case of $C_{60}[PhCNO]$ the bond lengths of the C1-C2, C2-C61, C61-C62 and C61-N are shortened, while the $\angle C2-C61-C62$ is the smallest at the dihedral angle of 90° . So the steric effect and the resonance stability are the largest due to the

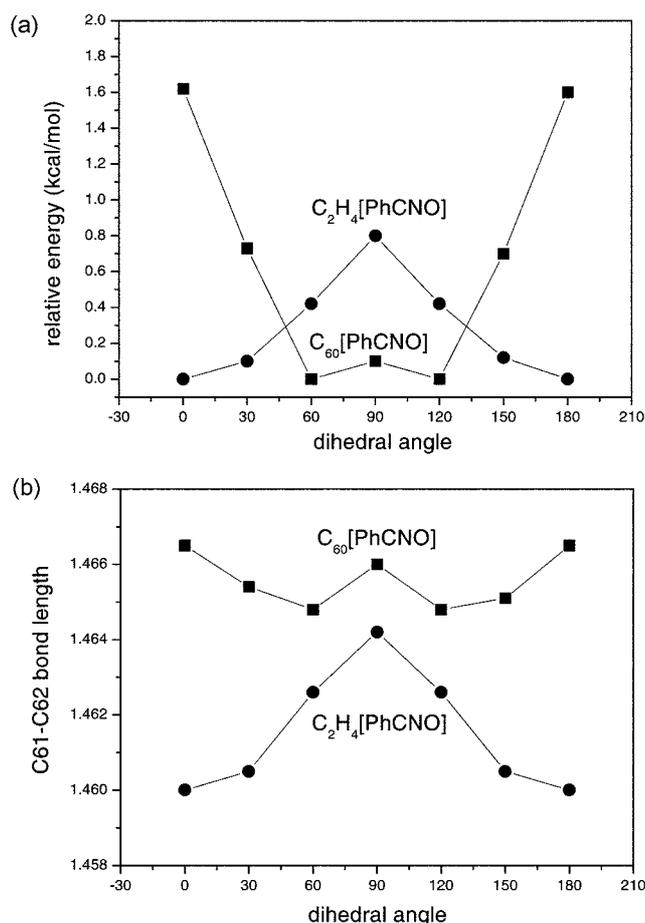


Figure 2. The comparison of the relative heats of formation (a) and the variations of the C61-C62 bond lengths (b) of $C_2H_4[PhCNO]$ (●) and $C_{60}[PhCNO]$ (■) according to the change of dihedral angle between the phenyl ring and the CNO planes.

geodesically stable and steric cage of C_{60} frame.

Figure 2(a) shows the comparison of the relative heats of formation of $C_2H_4[PhCNO]$ and $C_{60}[PhCNO]$ at each dihedral angle. Figure 2(b) shows the variations of the C61-C62 bond lengths in $C_2H_4[PhCNO]$ and $C_{60}[PhCNO]$ by the change of the dihedral angles. For the case of $C_2H_4[PhCNO]$ the bond length is shortest at the dihedral angle of 0°, but for the $C_{60}[PhCNO]$ at the angle of 60°. This suggests that the resonance effect mainly contributes to the stability given by the variation of the dihedral angles.

Diadduct: the relative stability of regioisomers. The binding of a bulky group PhCNO at one of 30 six-six ring fusions could sterically protect three of the surrounding 6-6 ring fusions. Thus we only considered five kinds of regio-

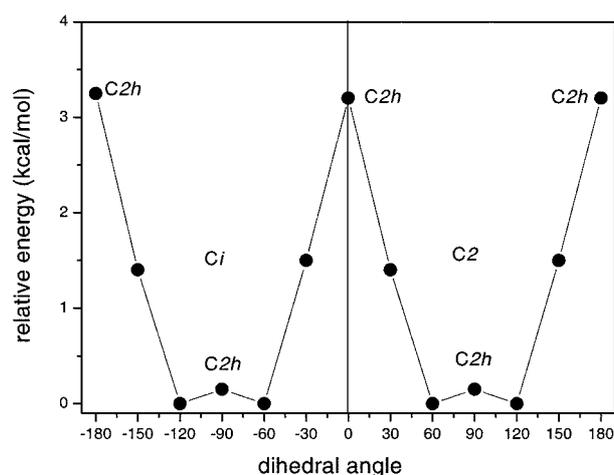


Figure 3. The relative stability according to the change of dihedral angle between the phenyl ring and the CNO planes in *trans-1* isomer.

isomers of eight possible diadducts. Also each regioisomer of diadduct could be formed in an obtuse or acute angle connection as shown in Scheme 3. Each connection could be formed in the same or opposite signs of two dihedral angles between the plane of phenyl ring and the plane of C2C61C62.

Table 3 shows the relative heats of formation (ΔH_f) in kcal/mol and the dipole moments (μ) in Debye for sixteen regioisomers obtained by using the PM3 calculations. The *equatorial* (*e*) regioisomers are the most stable among the diadducts. The obtuse connected *trans-3* regioisomer is the next most stable. Thus, *e* and *trans-3* isomers are the most preferable. The order of elution of thirteen isomers could correspond to the order of the calculated dipole moments. The least polar *trans-1* isomer would be the most soluble in toluene.

Meier and his coworkers³ recently reported that photo-diode array detection clearly showed approximately eight different isomeric species. Here, we could explain their experimental results by using our calculated dipole moments (unit: Debye), which are also grouped as follows: (0.2), (1.5, 1.8), (2.6), (2.9), (3.7), (3.9), (4.0), (4.4), (4.6). Our results also suggest that a dramatic simplification of the isomeric mixture at high temperature³ could be explained by the temperature dependence of polarizability of isomers, because the polarizability is proportional to the square of permanent dipole moment but is inversely proportional to the temperature.

The stability with the variation of dihedral angles in the *trans-1* regioisomer performed can be understood with the

Table 3. The calculated relative PM3 heats of formation (ΔH_f) in kcal/mol and PM3 dipole moments (μ) in Debye for all thirteen regioisomers with the obtuse and acute connection of $C_{60}(PhCNO)_2$ toward the same (opposite) rotational directions of two planes of phenyl rings

			obtuse angle connections			acute angle connections		
	<i>trans-1</i>	<i>e</i>	<i>trans-2</i>	<i>trans-3</i>	<i>trans-4</i>	<i>trans-2</i>	<i>trans-3</i>	<i>trans-4</i>
PM3 _F	0.5 (0.5)	0.0 (0.0)	0.6	0.2	0.4	0.6 (0.6)	0.3 (0.2)	0.5 (0.4)
PM3 _D	0.2 (4.4)	3.7 (2.6)	2.6	1.5	2.6	3.9	4.6	4.0

relative heats of formation shown in Figure 3. This result shows the same pattern as the monoadducts. The largest difference (about 3.25 kcal/mol) of the relative heat of formation of the diadduct is nearly double that (about 1.61 kcal/mol) of the monoadduct.

Our results suggest that fullerene isoxazoline derivatives could have the potential capability of nanoconnectors which attach spacer units in a specific angle arrangement.

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